# CHAPTER 3

# DEHYDROGENATION OF METHANOL TO METHYL FORMATE ON COPPER- EXCHANGED CLAY CATALYSTS.

## 3.1 INTRODUCTION.

The industrial production of methyl formate through methanol dehydrogenation has so far been hindered by the poor performance of catalysts, which generally exhibit low activity and moderate selectivity. Development of more active and specific catalysts may therefore lead to a commercially convenient utilization. In $C_1$ chemistry, methanol is interested as a feedstock for a wide range of organic chemicals , due to its easy transportation. Methyl formate is considered to be one of the key intermediates for methanol-based processes to produce acetic acid, dimethyl formamide, etc. For this advantage, an attempt was made to develop an active catalyst with high and prolonged activity and also with high selectivity for the dehydrogenation of methanol to methyl formate.

The efforts had been made to develop catalysts for the production of methyl formate by direct dehydrogenation of methanol. A survey of the patent literature indicated that consideration had been given on the improvement of copper-based catalysts for the production of methyl formate from methanol [77-81]. In the past, more attention had been paid to research on methanol dehydrogenation [82]. The effectiveness of various clays as supports and various metal cations exchange as catalysts were studied. Catalytic activities of Cu(II) ion exchanged forms of layer silicate clay minerals, including fluoro tetrasilicic mica (TSM) and zeolitic minerals had been investigated for conversion of methanol [83]. It was found that copper ion exchanged form of TSM seems to be the suitable catalyst for methanol dehydrogenation reaction. Consideration on the layer structure showed that TSM is of a laminate lattice silicate, face to face aggregation. This kind of structure gives a small interlayer space. The copper ions locating only on the outerlayer of TSM can catalyzed reactions of methanol because the interlayer space is too small for methanol molecules to enter and react with internal catalytic sites.

From this speculation, an idea to research on the other types of clay catalyst is created. The new type of clay catalyst should have a structure of delaminate layers, face to edge or edge to face aggregation. Then, the interlayer will be large enough for methanol molecules to enter and react with internal catalytic sites. Even though the selectivity of methyl formate may not be so high as Cu-TSM, because of some acid sites existing on the supporting clay. But the problem may be countermeasured by using such a modifier such as $Cr_2O_3$ or the other suitable modifiers. From this idea, the present research is attempted to develop an active catalyst with high activity and high selectivity for dehydrogenation of methanol to methyl formate.

## The Scope of This Research

1. Preparation of copper-exchanged clay catalysts by means of ion exchange on various type of silicate clay minerals such as sodium type of Laponite, Saponite, and Montmorillonite.

2. Study the effect of various factors on catalytic activity, selectivity, and stability such as

    a. Type of clay catalyst
    b. Reaction temperatures and reaction conditions
    c. Treatment temperatures
    d. Treatment atmospheres
    e. Degrees of copper ion exchange

3. Characterization of clay catalysts by means of
    a. Temperature Programmed Desorption (TPD)
    b. Surface Area Measurement
    c. Infrared Spectroscopy (IR)
    d. Inductivity Coupled Argon Plasma Atomic Emossion (ICP)
    e. X-ray Diffraction (XRD)
    f. Electron Spin Resonance (ESR)
    g. Pluse Measurement

## 3.2 EXPERIMENTAL

### 3.2.1 Type of Clay Catalysts

Smectite clay minerals used in this study are sodium-type natural montmorillonite, designated as Kunipia F, synthetic saponite and synthetic laponite obtained from Kunimine Industry Co. The chemical formula of each sodium-type clay is :

$Na_x[Al_{2-x}Mg_x](Si_4O_{10})(OH)_2.mH_2O$ ; Montmorillonite
$Na_x[Mg_3](Al_xSi_{4-x}O_{10})(OH)_2.mH_2O$ ; Saponite and
$Na_x[Mg_{3-x}Li_x](Si_4O_{10})(OH)_2.mH_2O$ ; Laponite.

In each formula the cations enclosed in branckets occupy octahedral sites and the cations in parentheses occupy tetrahedral sites. Saponite is tetrahedrally charged smectite with $Al^{3+}$ substituting for $Si^{4+}$. On the contrary, montmorillonite and laponite are octahedrally charge smectites with $Mg^{2+}$ substituting for $Al^{3+}$ and $Li^+$ substituting for $Mg^{2+}$, respectively. The substitution of metal ion in layered lattice silicate clays are shown in Fig. 3-1.

| Montmorillonite | Saponite | Laponite |
|---|---|---|
| $Si^{4+}$ | $Si^{4+} \leftarrow Al^{3+}$ | $Si^{4+}$ |
| $Al^{3+} \leftarrow Mg^{2+}$ | $Mg^{2+}$ | $Mg^{2+} \leftarrow Li^+$ |
| $Si^{4+}$ | $Si^{4+} \leftarrow Al^{3+}$ | $Si^{4+}$ |

Fig. 3-1 Substitution of metal ion in layer latticed silicate clays

### 3.2.2 Preparation of Copper-Exchanged Clay Catalysts

Copper-exchanged clay catalysts were prepared according to a conventional metal ion exchange method. A copper nitrate solution with a concentration of 0.01 N was prepared. A proper amount of copper nitrate [ $Cu(NO_3)_2.3H_2O$ , molecular weight 241.6 ] was solved in distilled water. A magnetic stirrer was used through mixing to obtained good performance of ion exchange. The solution was heated to a temperature of 50°c , 10 g of clay mineral was slowly added and continuously stirred for 24 hours at 50°c. Then the mixture was filtered and washed several times with distilled water to remove excess nitrate ions. Diphenylamine [ $C_{12}H_{11}N$ ], was used to detect nitrate ions in the filtrate, the preparation method of diphenylamine is shown in Appendix A. In an oven at 110°C, the precipitate was dried for 24 hours. The copper ion-exchanged produced will be abbreviated to Cu-Mont, Cu-Sapo, and Cu-Lapo in according to the type of clay minerals. The schematic diagram of synthesis of catalyst is shown in Fig. 3-2.

Copper cations in the nitrate solution were presented in large excess, typically 2 mmol $Cu^{2+}$ ions/meq.clay, to ensure complete saturation for exchangeable sites of $Na^+$ by $Cu^{2+}$. The excess concentration of copper nitrate solution used in the synthesis of catalyst is calculated on the basis of $Cu^{2+}$ 1 ions exchanged with $Na^+$ 2 ions including the consideration on cation exchange capacity (CEC). The details of calculation are shown in Appendix B.

To study the effects of the degrees of copper-ion exchange on the catalytic activity and selectivity of methyl formate formation in methanol dehydrogenation, the concentration of copper nitrate solution was varied. But the synthetic method of catalyst is still the same. The details of synthetic method of degrees of ion exchange will be mentioned in Appendix B.

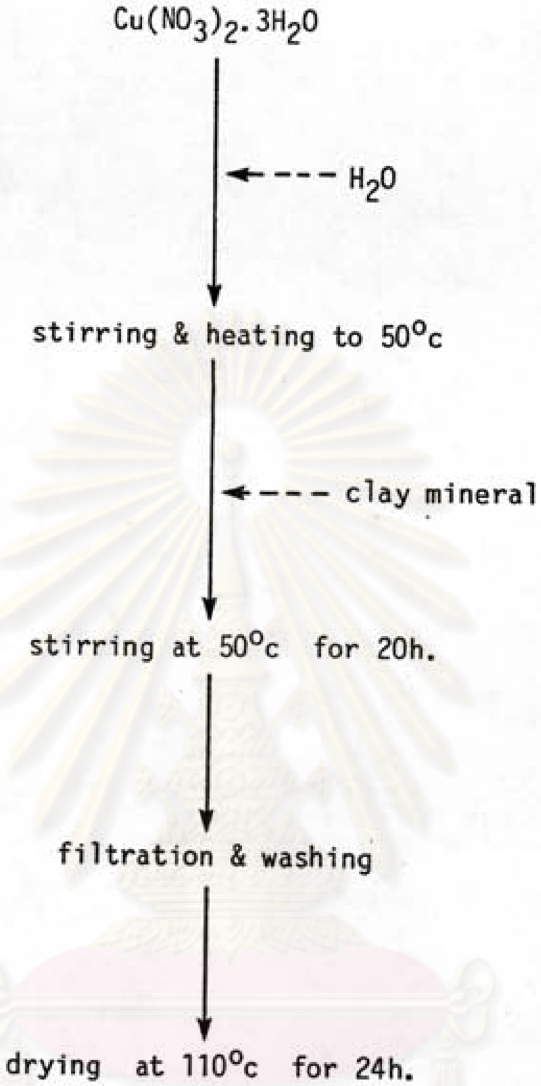
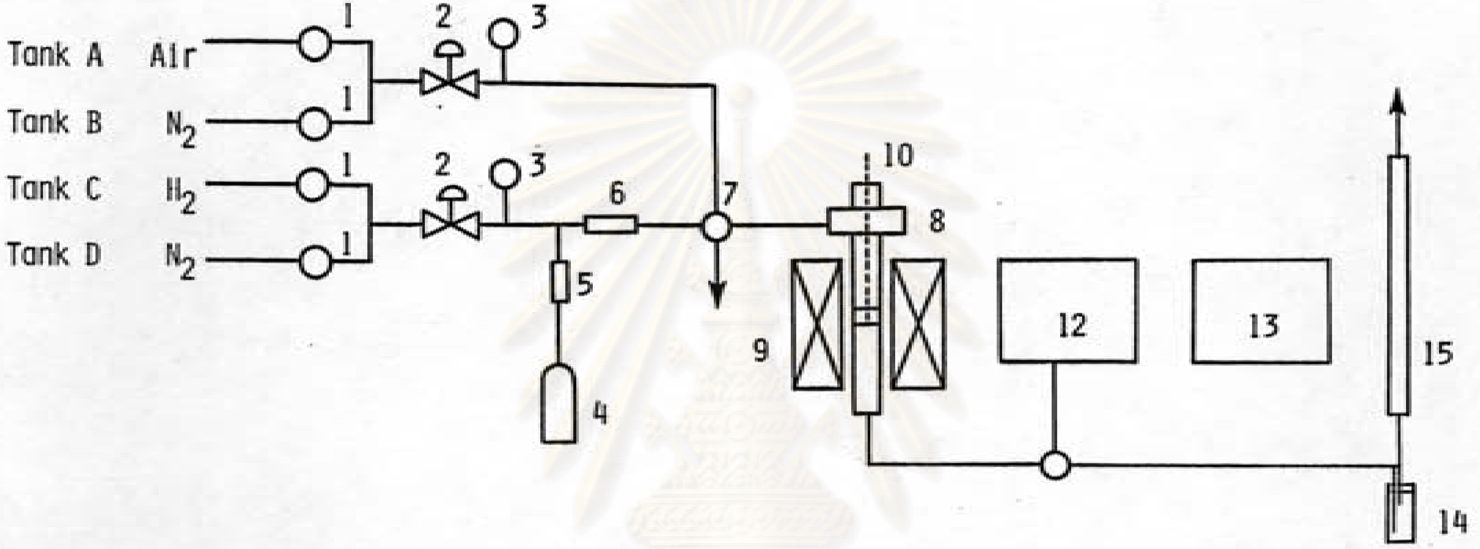


Fig. 3-2 Schematic diagram of synthesis of copper-ion exchanged clay catalyst.

### 3.2.3 Apparatus and Procedures

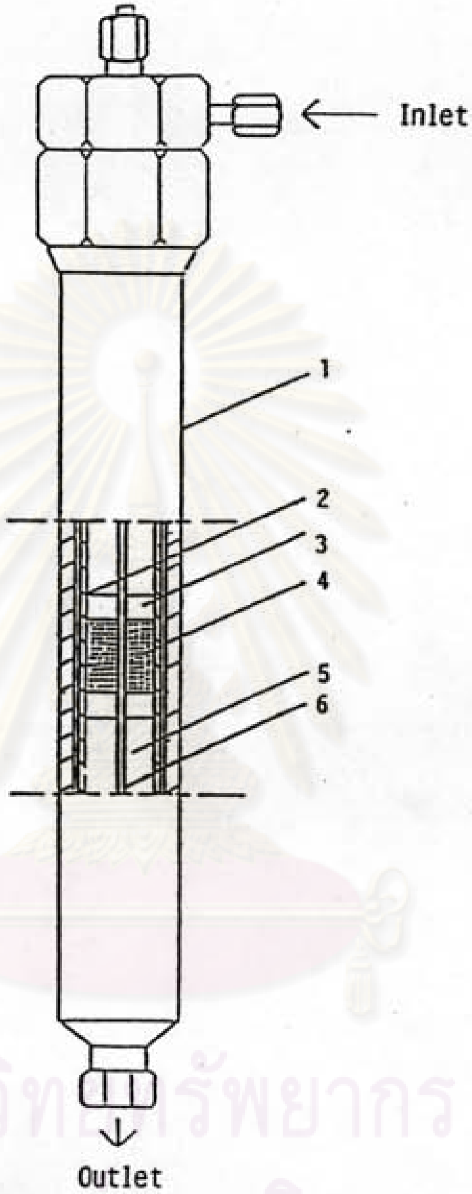
#### a. The experimental apparatus and reactor

Dehydrogenation of methanol was carried out at atmospheric pressure using a fixed bed continuous flow reactor equipped with a gas sampling valve for gas chromatographic analysis. The experimental apparatus is shown in Fig. 3-3 and the reactor is shown in Fig. 3-4. The reactor is made of a pyrex glass tube (20 mm o.d., 18 mm i.d. and 370 mm totally long). In the middle part of the reactor, the small size of pyrex tube(11 mm o.d., 9 mm i.d. and 100 mm long) is connected for the reason of enough contact time between reactant and catalyst. The pyrex glass reactor is mounted vertically in a steel tube covered by electrical furnace. An amount of 0.3 g of catalyst sample was packed between silica wool and glass beads at ca. 21 mm from the top of reactor where the highest temperature obtained. During test run of experimental apparatus, the calibration of temperature of reactor was done to find out the maximum point. At the center of reactor, thermocouple was inserted from the top of reactor until the middle of catalyst bed in small steel tube which was covered with pyrex glass 5 mm in diameter. Glass beads were filled in the empty space of the reactor tube to minimize the dead volume.



1. Stop valve
2. Gas flow valve
3. Pressure gauge
4. Microfeeder
5. Vaporizer
6. Mixer
7. 4-way cock
8. Reactor
9. Electrical furnace
10. Thermocouple
11. Gas sampling valve
12. GC-TCD : $H_2$
13. GC-TCD :Ar
14. Dry ice trap
15. Soap film meter

Fig. 3-3 Schematic diagram of experimental apparatus.



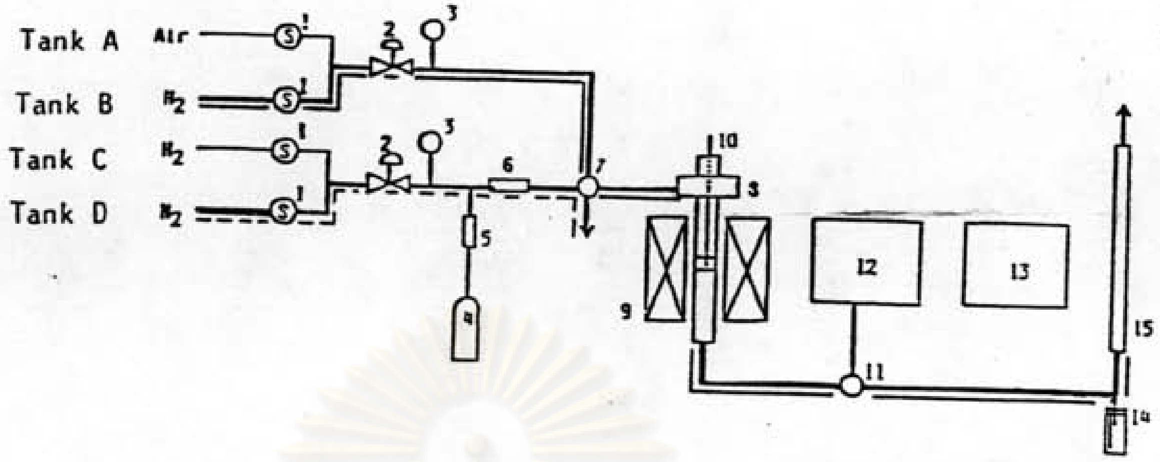
1. Steel tube    2. Pyrex glass reactor tube
3. Silica wool    4. Catalyst bed
5. Glass beads    6. Thermocouple

Fig. 3-4 Reactor

### b. Treatment and reaction conditions

Prior to the reaction, the catalyst was treated for 1 h at various temperatures in the range of 300°C to 500°C, in a stream of $N_2$ treatment gas passed from ~~Tank B through~~ treatment gas line. The treatment gas line and reaction gas line are shown in Fig. 3-5. The flow rate of $N_2$ gas was maintained at 65 cc/min measured by means of soap film meter(15). Then the gas line through the reactor was changed from treatment gas line to the reaction gas line by means of 4-way cock. Methanol was quantitatively supplied from a microfeeder(4) to the reactor(8) through a vaporizer(5). During test run of experimental apparatus, the calibration curve between dial of feeder and flow rate of methanol was done. $N_2$ gas from Tank D was used as the methanol-carrier gas. The molar ratio of methanol to nitrogen was 2:5. The reaction was carried out in the temperature range of 200°C to 300°C. The time factor was defined by a conventional reciprocal space velocity, W/F , as a ratio of catalyst weight(g.cat) to methanol flow rate (min/mol) being ranged from 100 to 2000 g-cat.min/mol.

Treatment



Reaction

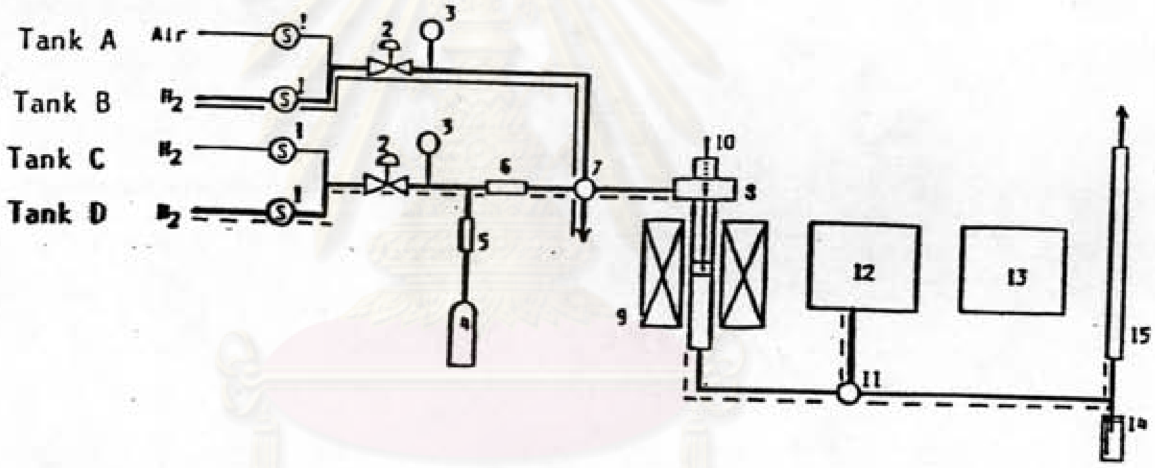


Fig. 3-5 Treatment and reaction gas line in experimental apparatus.

treatment gas line - - - - - - -

reaction gas line ————

### c. Analysis of products

The reaction products were analyzed in two samplings. In the first sampling, the effluent gas was directly plused by a 6-way cock gas sampling valve to gas chromatograph(GC)(12) for on-line analysis of the reac~~tion products.~~ In GC (12), a series of porapac T and Q packed columns as an analyzing column and porapac Q packed column as a reference column in a stainless steel tube, 3x4 mm in diameter and 3 m length, were mounted with thermal conductivity detector(TCD). The details of GC are shown more in Appendix C. $H_2$ from the other storage tank was used as carrier gas and flow rate of $H_2$ was maintained at 40 cc/min. The components of the effluent gas viz. $N_2$, CO, $CO_2$, $H_2O$, $H_3COCH_3$, $CH_3OH$ and $HCOOCH_3$ were analyzed at a temperature of 100°C in about 40 minutes. The retention time and peak area of each product was recorded by the recorder as shown in Appendix D.

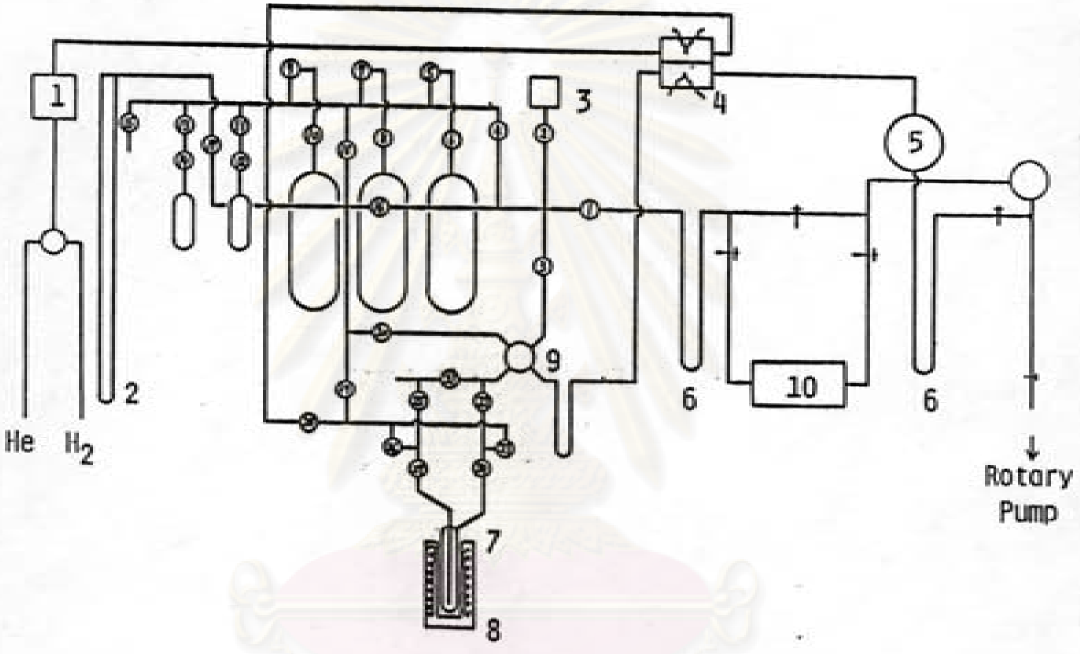
In order to eliminate the contribution of high boiling point products such as methanol, methyl formate, dimethyl ether and water in the GC analysis of the second sampling, a trap immersed in a dry-ice mixed with methanol bath was setted between 6-way cock and the second sampling point before the soap film meter. The second sampling of the outgases after dry ice-trap of the effluent gas was collected by syringe. The sampling gas of 0.5 ml was injected in another gas chromatograph(13), in which a 3x4 mm in diameter stainless steel tube packed with active carbon was used and the carrier gas was argon. The flow rate of argon was maintained at 40 cc/min. $H_2$, $N_2$, CO, $CH_4$, and $CO_2$ were analyzed at a temperature of 100°C in about 5 mins. The flow rate of the outgases was measured by use of a soap flim meter(14) and room temperature was recorded at each sampling. In every sampling, peak area of air was measured by injection of air 0.5 ml to GC(13). During analyzing, the flow rate of carrier gas and temperature of GC were maintained at constant values. The analytical data obtained from GC were presented in peak area of each product and then calculation was done to interprete the results in terms of % conversion and % selectivity on a carbon mole basis. The raw data, data sheet and calculation method are also shown in Appendix D.

### 3.2.4 Characterization of clay catalysts

#### a. Temperature Programmed Desorption (TPD) measurement

TPD measurements were performed to characterize the acidic properties of catalysts. A thermal conductivity detector (TCD) with He carrier gas was used to detect the desorbed ammonia ($NH_3$). An apparatus used in TPD measurements is shown in Fig.3-6. The data were collected with points taken at 6 seconds interval, which were signals of both concentration of desorbed $NH_3$ and temperature changes. These signals were amplified and then sent to Shimadzu chromatopac model C-R2AX for data storage, processing and plotting.

In TPD measurements, a catalyst in the mesh size of ca. 0.5 g was accurately weighed and placed in the cell as shown in Fig. 3-7. A time and temperature programmed controller was used throughout the measurements. The schematic diagram of time and temperature of $H_2O$ and $NH_3$ desorption measurements are shown in Fig. 3-8. The system was evacuated by used of a vacuum rotary pump and the sample was treated at 400°C for 1 hr in vacuo and then the sample was cooled to 100°C. When the stable temperature at 100°C obtained, $NH_3$ gas of 100 Torr was introduced to catalyst sample. $NH_3$ adsorption was done for 30 min, and excess $NH_3$ was evacuated for 30 min. Prior to measurement of $NH_3$ desorption, the sample was cooled down to 50°C and kept in a stream of He (100 Torr and 44 cc/min in flow rate) to attain the steady flow. The measurement was carried out at a heating rate of 10°C/min, conducted from 50°C to 500°C. Since at the temperature region above 400°C, a considerable amount of water which produced from dehydroxylation was desorbed. The spectrum of desorbed water, named background, was separately detected for the sample which had not adsorbed ammonia. The $NH_3$-TPD spectrum was obtained by point-to-point substraction of $H_2O$ desorption spectrum from $NH_3$ desorption spectrum. The details of vacuum, He and $NH_3$ line during treatment, NH3 adsoption and measurement are shown in Fig. 3-9.

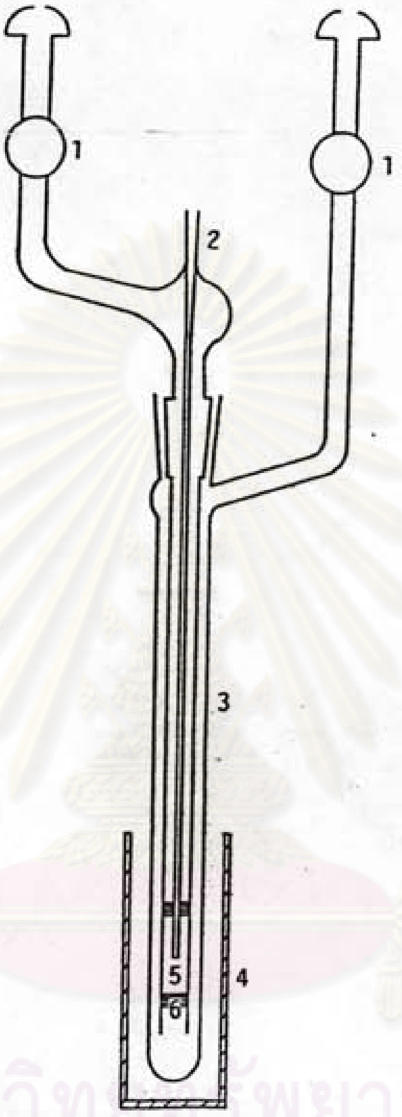


1. Gas Flow Controller
2. Hg Manometer
3. Ionization Guage
4. Thermal Conductivity Detector
5. Buffer
6. Liquid $N_2$ Trap
7. Oil Diffusion Pump
8. Sampling Cock
9. $NH_3$ Glass Storage Tank
10. TPD Sampling Cell
11. Electric Furnace

① - ㉘ Stop Valve

† Cock.

Fig. 3-6 Scheme of Temperature Programmed Desorption Apparatus



| | |
|---|---|
| 1. Cock | 2. Capillary tube for thermocouple |
| 3. Pyrex tube | 4. Heater |
| 5. Catalyst bed | 6. Silica wool |

Fig. 3-7 TPD cell.

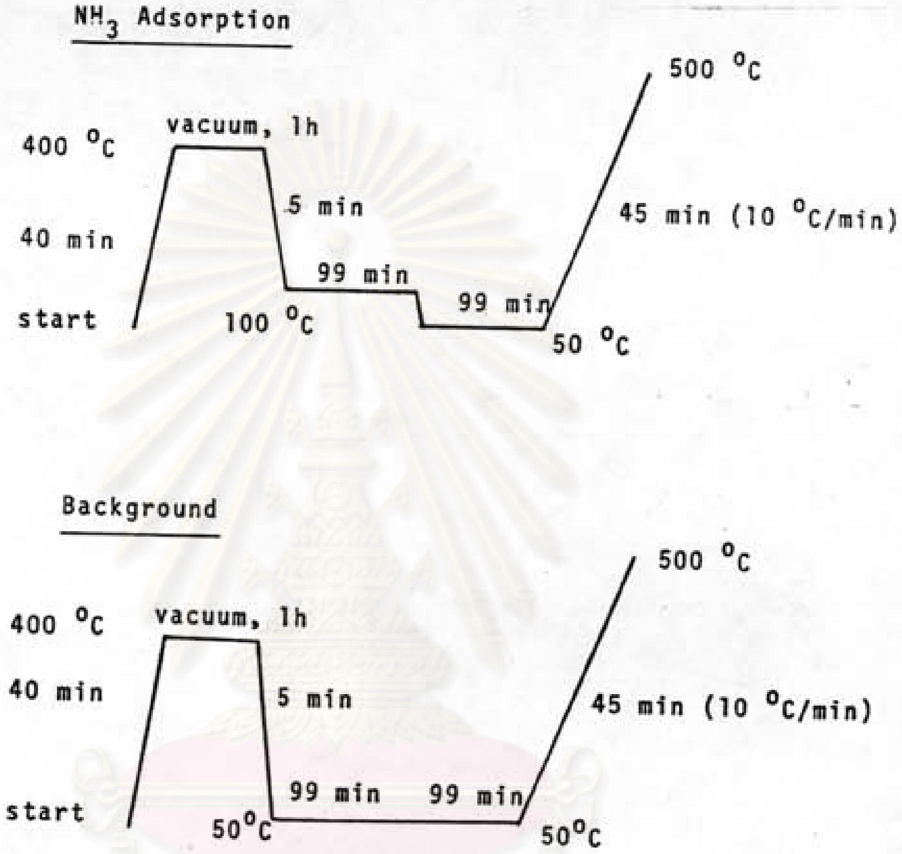
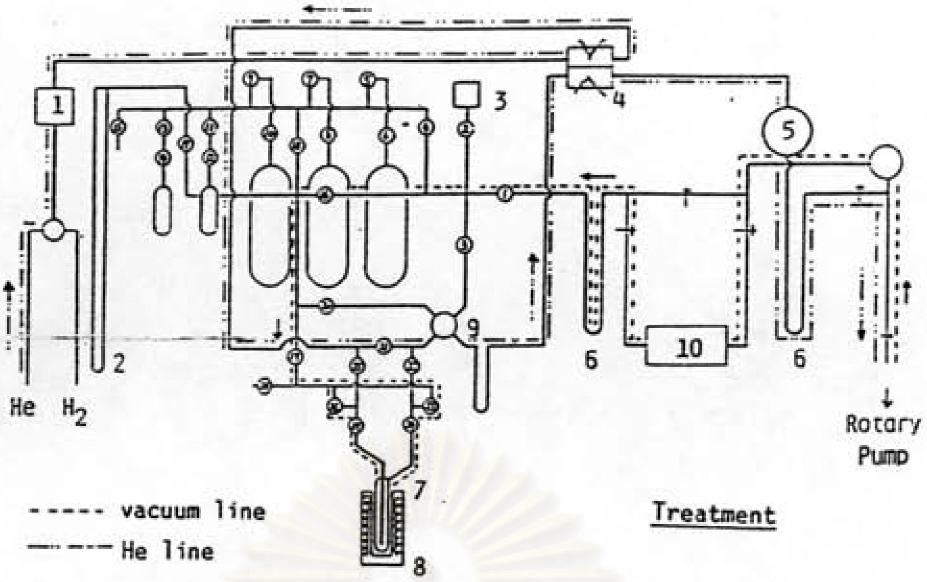
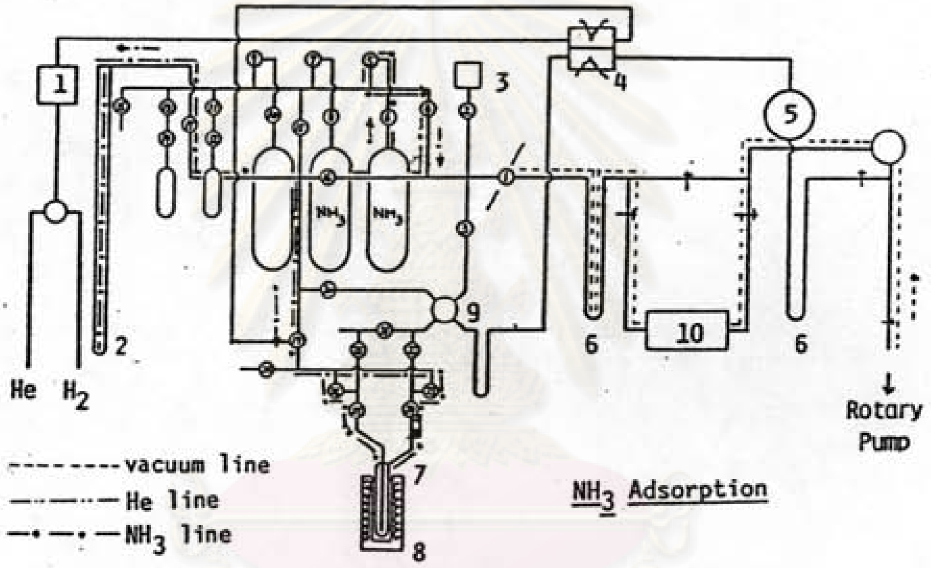


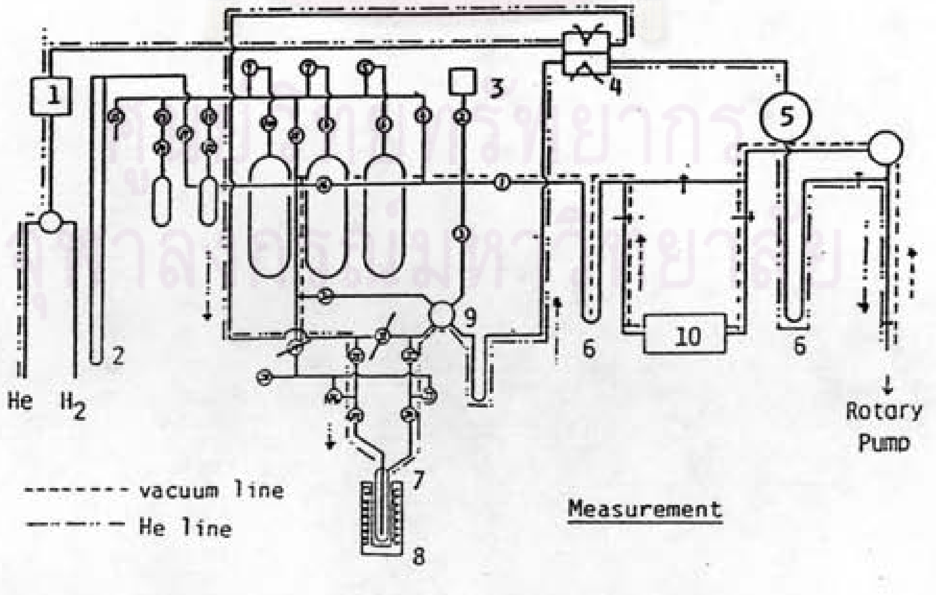
Fig. 3-8 Schematic diagram of time and temperature for TPD measurements.



Treatment



$NH_3$ Adsorption



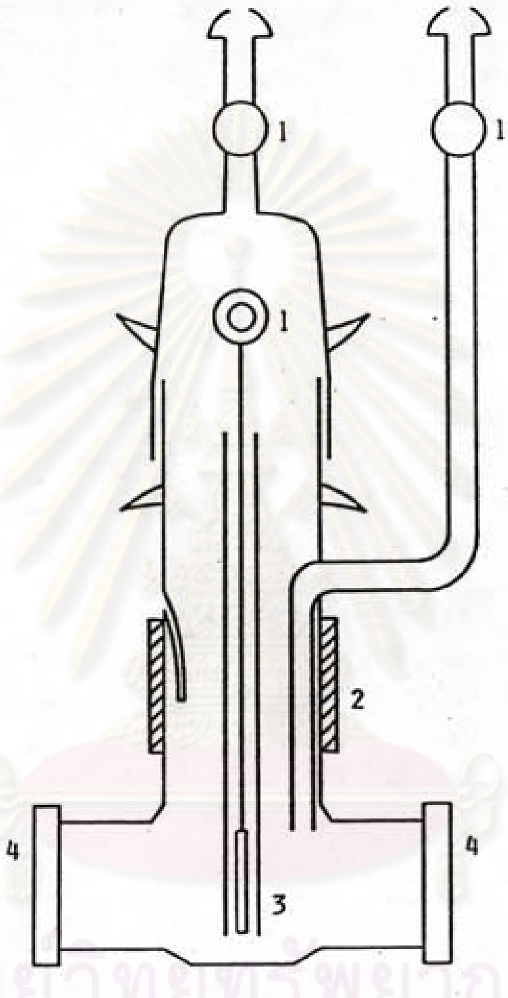
Measurement

Fig. 3-9 The details of vaccum line, He line, and $NH_3$ line during treatment, $NH_3$ adsorption and measurement.

### b. Infrared Spectroscopy (IR) measurement

Infrared spectroscopy has become a valuable tool for the determination of structural information concerning organic substances. Its application to organic systems has been in the areas of both quantitative and quanlitative analysis. Quanlitative analysis has been by far the greatest application of this valuable tool in organic chemistry.

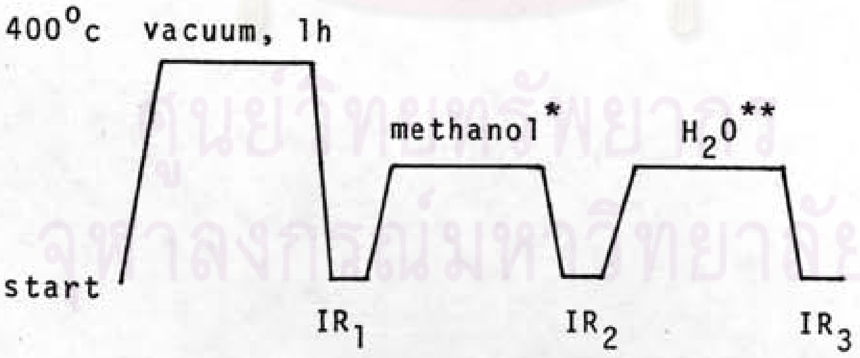
In this research, IR was used to characterize the effect of $H_2O$ to the absorption of methanol on catalyst. And also the characterization of $Cu^+$ ion on catalyst by the adsorption of carbon monoxide (CO). In some researches, the acidic properties of catalysts were characterized and the adsorption of pyridine monitered by infrared spectroscopy was used to distinguish the Bronsted and Lewis acid sites. An IR spectrum was recorded on a diffraction grating infrared spectrophotometer modle IR-810 Jasco (Japan Spectroscopic Co., Ltd.). A catalyst sample was pressed at 400 $kg/cm^2$ into a self-supporting wafer (20 mm in dia and ca 30 mg). The wafer was then mounted in a quartz sample holder and placed in the infrared cell, in which the KBr wafer disc technic was employed. Fig. 3-10 shows the infrared cell. A quartz sample holder was connected by a platinum wire to a cock which held the holder up and down during heating and measuring. The measurement was carried out at room temperature and a wafer of catalyst was placed parallel to the KBr windows.



1. Cock  2. Heating section
3. Sample wafer  4. KBr window

Fig. 3-10 Infrared cell.

An apparatus used in IR measurements is the same in principle as that of $NH_3$ absorption measurements as shown in Fig. 3-6. The wafer sample was evacuated at 400°c for 1 hr by use of vacuum rotary pump in vacuo and then cooled down to room temperature. An IR spectrum, named background, was recorded. The temperature was again raised up to 200°C as same as reaction temperature and methanol was introduced from a small glass storage to a catalyst. Methanol adsorption was done for 30 min, and excess methanol was evacuated at the same temperature for 30 min. Then the second IR spectrum was recorded at room temperature. Again the temperature was raised up to 200°C and $H_2O$ was absorped for 30 min in vacuo and the excess $H_2O$ was desorped for another 30 min in the same condition. The IR spectra was recorded at room temperature. In interpreting the data, IR spectrum of each measurement was elaborated by the IR background spectrum and the results were modified both in % absorption and in % transmittion. The schematic diagram of time and temperature in IR measurement is shown in Fig. 3-11.



* = methanol adsorption 30 min and desorption 30 min

** = $H_2O$ adsorption 30 min and desorption 30 min.

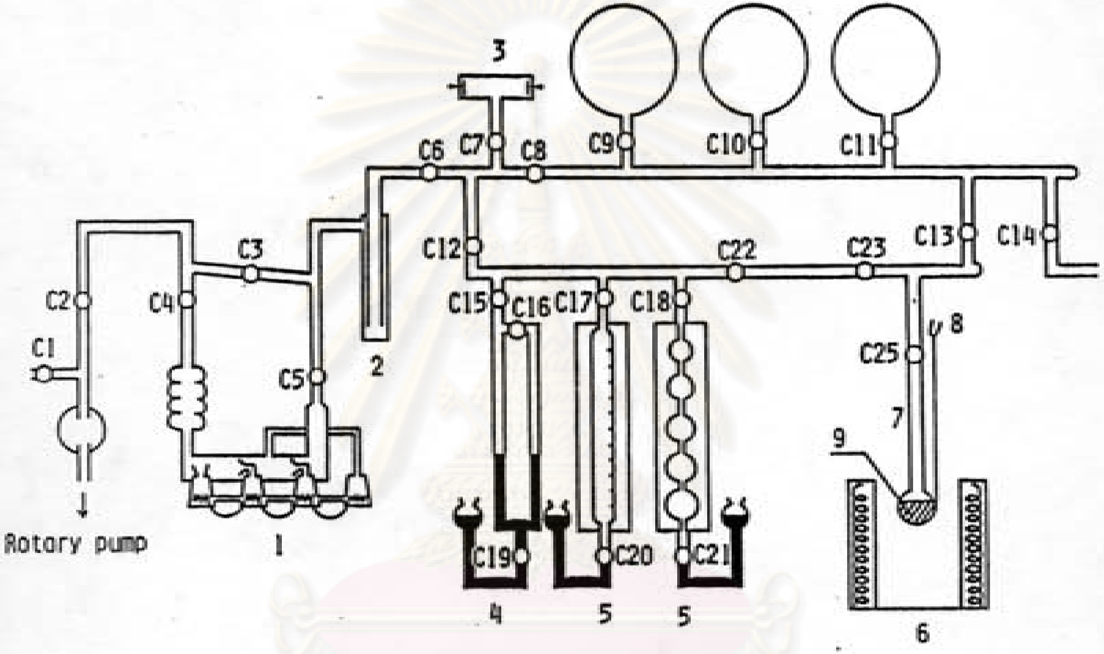
Fig. 3-11 Schematic diagram of time and temperature of IR measurement.

### c. Surface area measurement

Surface area of a catalyst was determined from a nitrogen ($N_2$) adsorption isotherm using a Langmuir or BET (Brunauer, Emmett, Teller) equation. $N_2$ adsorption was measured at -196°C, in a liquid $N_2$ trap, by using a conventional high vacuum static system as shown in Fig. 3-12. A catalyst of 0.1 g was weighed and loaded in a sample-glass cell. The silica wool used in this measurement was also weighed. The system was evacuated and leak-checking was done for 15 min prior to evacuation in vacuo at 200°C for 1 hr. Time and temperature were controlled by using a temperature programmed controller. The sample was cooled down to room temperature, then the measurement were done in the main 4 steps :

1. Introduction of He gas into the system and amount of He charge into the system was calculated.
2. Introduction of He gas into the sample-glass cell, on the other hand, into the catalyst and dead volumn (total volumn of catalytic cell) was calculated. Note : at -195.8°C He does not adsorp on catalyst due to the gaseous state.
3. Introduction of $N_2$ gas into the system and amount of $N_2$ charge was calculated.
4. Introduction of $N_2$ gas into the catalyst and amount of $N_2$ absorped on catalyst was calculated.

In each step of measurements, the difference in levels of Hg in manometer and room temperature were recorded. During introduction of He or $N_2$ into the catalyst, the sample-glass cell was dipped into the liquid $N_2$ trap to control the constant rate of absorption. From the calculated amount of $N_2$ absorped, these data were fit by Langmuir or BET equation, depending on the structure of catalysts, to calculate for the total area of absorption. Finally, the surface area of catalyst was calculated. The detail of calculations are shown in Appendix E.



1. Oil diffusion pump
2. Liquid $N_2$ trap
3. Induction coil
4. Manometer
5. Burette
6. Electric furnace
7. Sample cell
8. Thermocouple
9. Sample

C1-C25 Cock

Fig. 3-12 Apparatus for adsorption measurement

### d. Inductivity Coupled Argon Plasma Atomic Emission Spectrophotometer(ICP).

ICP was used to characterize the amount of various metal ions on a catalyst. In the present study, the amounts of Na and Cu ions in clay catalysts were determined. The analyzing apparatus was Nipon Jarrel-Ash model ICAP-575 mark II.

### The preparation of sample solution.

Clay catalyst of 0.2 g was weighed and solved with concentrated solutions of HF 10 ml and $H_2SO_4$ 1 ml. Teflon pipet and beaker were used while using HF was concerned. Then the mixture was heated for about 2 hr at 110–160°c on a hot plate in a drafter until HF and $H_2SO_4$ were all vaporized. After that concentrated HCl solution of 5 ml was filled into the mixture to form metal chloride. Finally, distilled water was filled to the mixture within a 100 ml volumetric flask. Fig. 3-13 showed schematic diagram of preparation method of sample solution.

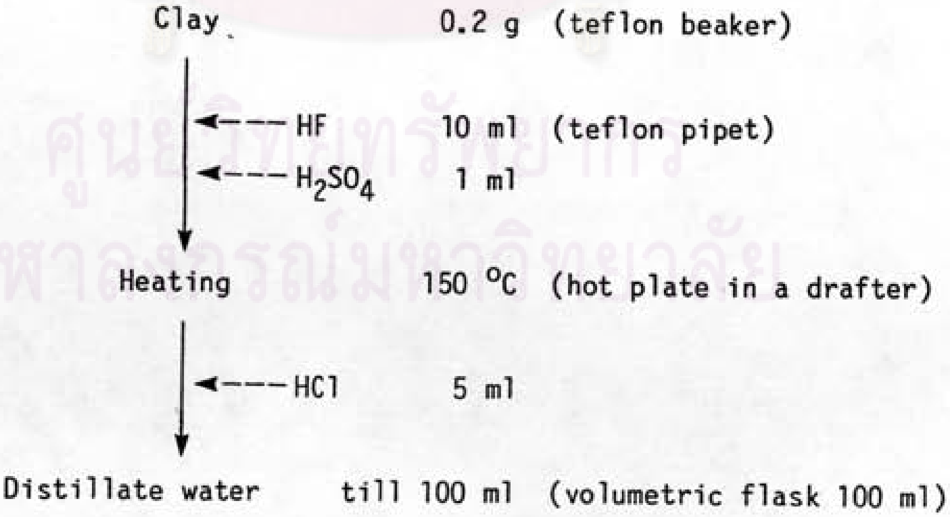


Fig. 3-13 Schematic diagram of preparation method of sample solution.

The preparation of standard solution.

The standard solutions of each analyzing ion was prepared by diluted from the 1000 ppm standard solution. Two difference ranges of concentration which covered those of sample solutions, were prepared. The blank solution was prepared in the same way as sample solution without the addition of catalyst.

Measurement.

The prepared solution was introduced into ICAP mark II for data storage, processing, and interpreting by means of a computer program. At first, the concentrations of standard solution were measured and standard curve was plotted. Then the sample solution was introduced into ICAP Mark II by the conveying tube to the flame for analysis. The data were elaborated in terms of amount of metal ions per 100 ml of solution using 0.2 g of catalyst ( mg.metal ions/ 100 ml solution/0.2 g catalyst). The data of ICP measurement are shown in Appendix F.